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The Surface Temperature of
Ammonium Perchlorate
Burning at Elevated Pressures

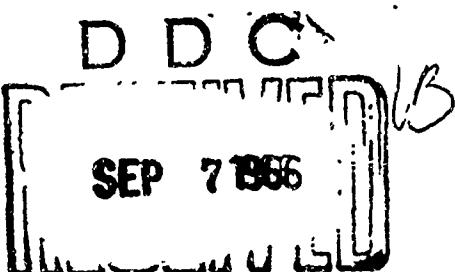
J. Powling
W. A. W. Smith

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(6) The Surface Temperature of
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Burning at Elevated Pressures,

(10) J. Powling and W. A. W. Smith

Foreword

The dependence on ambient pressure of the surface temperature of a burning ammonium perchlorate/fuel mixture provides important evidence for the mechanism of burning of composite propellants. However, the measurement of burning-surface temperature is extremely difficult because of the steep temperature gradient at the surface. This paper describes an infrared emission technique for measuring surface temperature which confines the measurement to a surface depth of as little as 2 microns. Experimental results are given for ammonium perchlorate/paraformaldehyde mixtures up to a pressure of 300 psia but even with this method temperature gradients above 60 psia were too steep for accurate results.

P. R. Freeman

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(11) June, 1966

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THE SURFACE TEMPERATURE OF AMMONIUM PERCHLORATE BURNING AT ELEVATED PRESSURES

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Measurements of the burning-surface temperatures of fuel-weak ammonium perchlorate/paraformaldehyde mixtures have been made up to pressures of 300 psia, using an infrared emission technique. Temperature determinations up to 60 psia were reasonably reproducible, the values being compatible with the existence, at the surface, of an equilibrium between solid ammonium perchlorate and the gaseous decomposition products, NH_3 and HClO_4 . Results above 60 psia were rather erratic, and failure to eliminate the variations by experiment led to an examination of the natural limitations of the optical method for measuring the surface temperatures of fast-burning compositions. The temperature gradients within the solid became too steep even for this method, which can "see" as little as 2 microns of surface depth.

Introduction

A method of measuring the surface temperature of burning-propellant ingredients by an infrared emission technique,¹ and its application to the problems of ammonium perchlorate deflagration at pressures within the range 760 to 20 mm Hg has been reported.^{2,3}

It would be of some interest to know how the surface temperature of ammonium perchlorate changed as the pressure increased beyond atmospheric towards rocket-operating pressures. In particular, it would be useful to see if any departure from the low-pressure relationship between surface temperature and pressure could be detected. At subatmospheric pressures, the burning-surface condition could be represented by the equilibrium



$$\Delta H_s = 56 \text{ kcal/mole}, \quad (1)$$

and the following relationship was valid:

$$\ln(K_{p1}/K_{p2}) = \ln(P_1^2/P_2^2) \\ = \Delta H_s(1/T_2 - 1/T_1)/R, \quad (2)$$

where K_p = equilibrium constant for Reaction (1) = $P_{\text{NH}_3} \times P_{\text{HClO}_4}$; P = ambient pressure; ΔH_s = heat of dissociation, Reaction (1); T = surface temperature, °K. Such a condition may not continue to apply at elevated pressures, when eventually the surface temperature would be required to approach the flame temperature of the reaction between NH_3 and HClO_4 and the partial pressures of these products at the surface would approach zero.

The present paper describes the development of the infrared optical method for measurement of the surface temperatures of ammonium perchlorate burning at elevated pressures and some results are given for very weak fuel/perchlorate mixtures. The natural limitations of the technique are indicated.

Experimental Method

To be able to measure the surface temperature of a deflagrating substance by a radiation method it is necessary to obtain a measure of the intensity of radiation from the surface without contribution from the enveloping hot gases and, additionally, to have knowledge of the emissivity of the thin radiating surface layer.¹ Both of these requirements become progressively more difficult to fulfil experimentally as the ambient pressure rises. The flame-gas density, and hence the gas emissivity, increases with increase of pressure and it becomes difficult to "see through" the flame envelope, particularly as the increasing rate of production of gas makes physical removal of these flame gases more difficult.

The equipment described previously¹ was modified in the following way: The low-pressure combustion chamber was replaced by a constant pressure bomb in which a strong flow of inert gas could be maintained counter to the flow of flame gases from the burning-propellant surface. The propellant surface could be viewed through an infrared transmitting window, protected by the same flow of inert gas. Figures 1 and 2 outline the essential features of the bomb. The optical system, infrared monochromator, and reference blackbody were similar to those

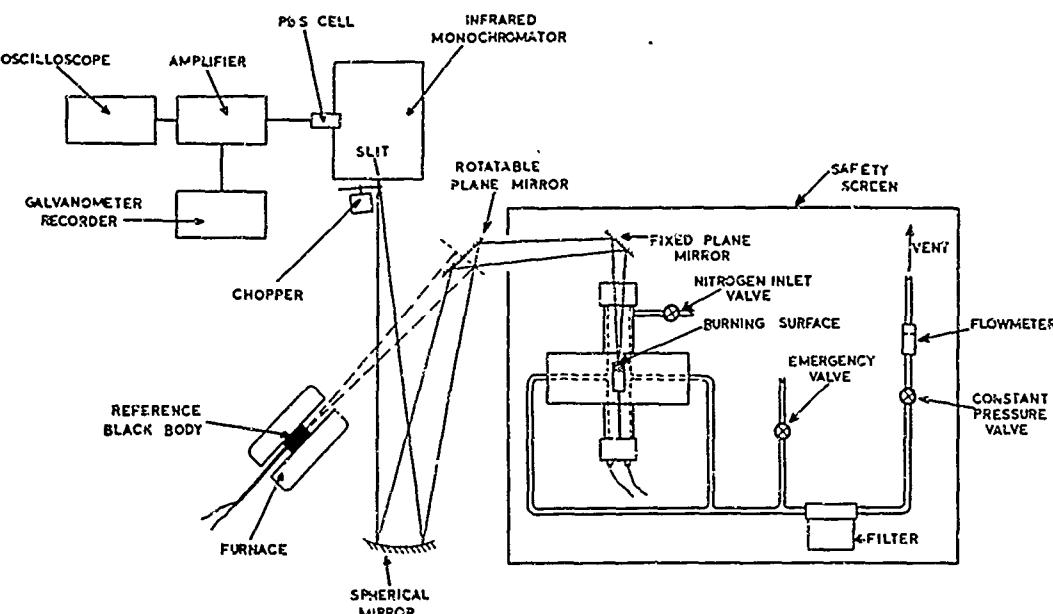


FIG. 1. Layout of apparatus.

described previously; but, because of time restrictions imposed by high burning rates, a faster infrared detector (lead sulfide cell) was required. The radiation was chopped at 1250 cps, and the output from a tuned amplifier displayed on a cathode-ray tube or recorded with a galvanometer recorder. Of the wavelengths favorable for surface-temperature measurements of burning ammonium perchlorate, only that at 3.1 microns was within the useful range of the PbS cell. Therefore, all measurements were carried out at this wavelength. The surface temperatures were calculated using Planck's Law, from the relationship

$$\left(\frac{J_a}{J_b}\right)_\lambda = \frac{\epsilon_a \lambda [\exp(C_2/\lambda T_b) - 1]}{\exp(C_2/\lambda T_a) - 1}$$

$$T_a = 0.625/\lambda \log \{ (J_b \epsilon_a / J_a)_\lambda \times [\exp(C_2/\lambda T_b) - 1] + 1 \},$$

where J is the spectral radiant intensity (corrected as necessary for window transmission and mirror reflection losses and gas emission or absorption), λ the wavelength in cm, ϵ the emissivity, C_2 the second radiation constant (1.439 cm deg), T the temperature in °K, a the ammonium perchlorate surface, and b the blackbody.

Establishment of desirable burning conditions within the bomb was difficult because the requirements for prompt ignition of the propellant surface were diametrically opposed to those necessary for low emission from the gas phase: compositions giving low gas temperatures were difficult to ignite when a stream of nitrogen was directed against the surface, "hotter" composition had low effective surface emissivities (see

later) and gave troublesome gas emission. No completely satisfactory means of igniting "cool"-fuel/ammonium perchlorate mixtures was found; the best was a fuse-wire embedded in a thin layer of a fast-burning plastic propellant placed over the surface of the composition. Irregular burning, resulting from failure to ignite the whole surface area at once, made elimination of the gas-phase emission difficult, as did cone-burning of inadequately inhibited pressed pellets or hollow burning of excessively inhibited samples. Exact control of burning surface after ignition was not always possible in strong counterflows of nitrogen.

Results and Discussion

The surface temperatures for some weak paraformaldehyde/ammonium perchlorate mixtures burning at pressures up to 300 psi are shown in Fig. 3. The change of surface temperature with pressure, from 15 psia to 60 psia, was in accord with the predictions from results at sub-atmospheric pressure,³ from which it was possible to deduce that the process taking place at the ammonium perchlorate surface during burning was most probably the reaction



with near-equilibrium conditions existing between the solid and gaseous phases. Up to 60 psia, the surface temperature and the ambient pressure can still be related through Eq. (2), but above this pressure the scatter of temperature values is too great for positive conclusion, although the latter continue to follow the trend of the low

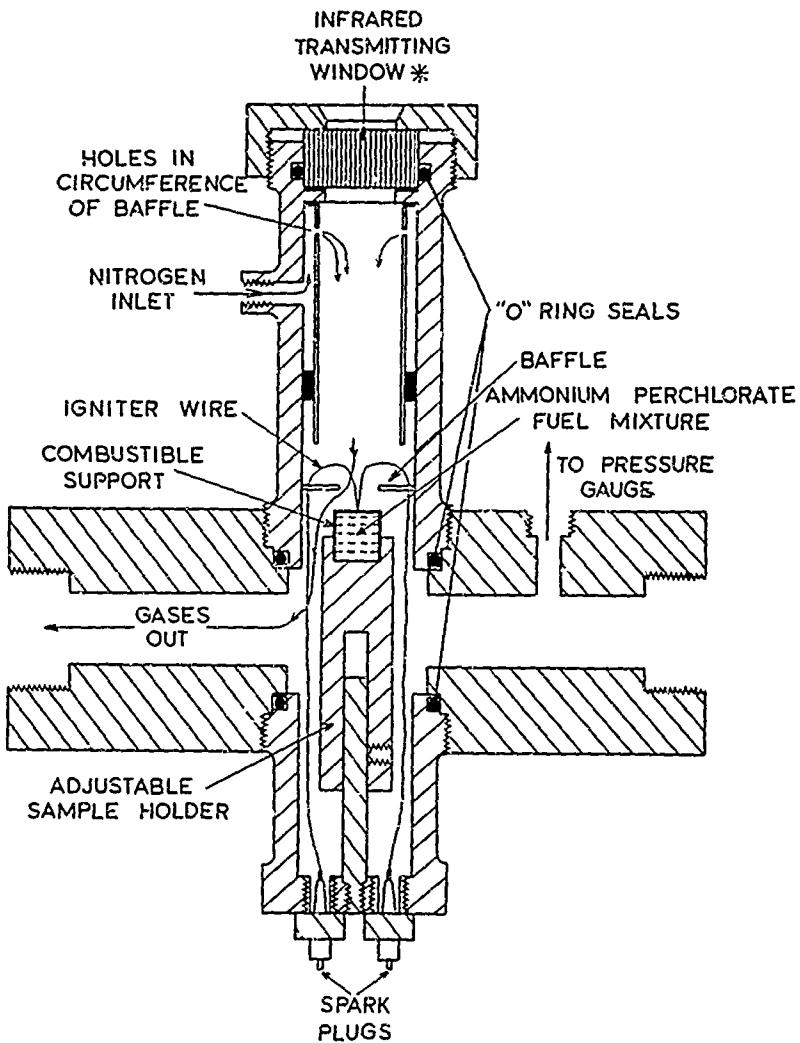


FIG. 2. Details of high pressure burner. Note: infrared window, 0.75-in.-thick Barr and Stroud BS 37A glass.

pressure results. Figure 4 shows the pressure/reciprocal-surface-temperature relationship over a wide range of pressure, the line being based on the low-pressure results of the previous work. Extrapolation to rocket-operating pressures, although a procedure of questionable value, would give ammonium perchlorate-surface temperatures of $\sim 650^\circ\text{C}$ at 300 psi, $\sim 680^\circ\text{C}$ at 500 psi and $\sim 720^\circ\text{C}$ at 1000 psi. These may be compared with an earlier estimate of $\leq 816^\circ\text{C}$ at 500 psi made by Friedman, Levy, and Rumbel,⁴ who also used a radiometric method but in a wavelength region in which the absorptivity of ammonium perchlorate is very low. They discussed the limitations of their assumptions, concerning the emissivity of the salt and the gas emission, but the present results suggest that these factors had been underestimated.

High-pressure surface temperatures have been estimated by Nachbar⁵ from linear pyrolysis of results of Andersen and Chaiken⁶ and burning-

rate/pressure data.⁴ Values at 1000 and 500 psi would be $\sim 830^\circ$ and $\sim 780^\circ\text{C}$, respectively. No agreement between their values and ours would be expected because theirs were derived assuming kinetic decomposition of the surface layer, the rate of regression of the surface being controlled by its temperature.

More recently, attempts have been made⁷⁻⁹ to arrive at the burning-surface temperature of ammonium perchlorate-based systems using thermocouples.

McAlevy and Lee⁷ have discounted the hypothesis of (near) equilibrium between solid ammonium perchlorate and its dissociation products on the strength of temperature/time records obtained with thermocouples made from 25- $\mu\text{-diam}$ wires. Their (low-pressure) deflagration rates were such that the temperature gradients were not excessive relative to thermocouple dimension but the present authors have serious doubts concerning the location of the true surface

on the method imposed by the increase of gas emission, which masks the emission from the surface, and the decrease of the effective emissivity of the surface when the temperature gradient within the surface becomes large (at high rates of burning). The following assumptions and conditions have been applied to make the treatment simple:

(i) The ammonium perchlorate-burning surface is planar and the temperature gradient within it (Fig. 5, inset) is described by:

$$T_x - T_0 = (T_s - T_0) \exp(-\dot{m}cx/\kappa)$$

where T_0 is the temperature of unburned composition ($^{\circ}\text{K}$), T_x the temperature at distance x cm within the surface, T_s the surface temperature, \dot{m} the mass rate of burning per unit of surface area, c the heat capacity of the solid (0.25 cal/g $^{\circ}\text{C}$ assumed), and κ the thermal conductivity of the solid (7×10^{-4} cal/cm sec $^{\circ}\text{K}$ assumed).

(ii) The effective emissivity of the burning surface required for the determination of T_s is arbitrarily chosen to be that of surface layer, x cm thick, within which the temperature has not fallen by more than 5 per cent of T_s . That is, ϵ_x for the condition

$$(T_x - T_0)/(T_s - T_0) = 0.95.$$

Then

$$\epsilon_x = \epsilon [1 - \exp(-kx)]$$

where ϵ_x is the emissivity of layer x cm thick, ϵ the measured emissivity for opaque layer, and k the absorption coefficient of ammonium perchlorate at the appropriate wavelength.

(iii) The thickness of the envelope of hot gases surrounding the burning surface cannot be reduced to less than 0.2 cm in the high-pressure experiments. This thickness is taken as constant in estimating the gas emission as a function of pressure. Rough measurements of the flame-gas emission from some weak paraformaldehyde/ammonium perchlorate compositions were made at atmospheric pressure and the emissivities at higher pressures calculated from these. Where temperature changes were known to occur with pressure increase (e.g., 5 per cent paraformaldehyde/ammonium perchlorate), they were taken into account. Since the measurements at elevated pressure are limited to one wavelength, the possible contribution of chemiluminescence from the gaseous reaction zone cannot be readily estimated. It is not judged to be serious but would, if present, give rise to spuriously high surface temperatures.

The change of depth of the surface layer x [for the condition $(T_x - T_0)/(T_s - T_0) = 0.95$] with pressure is indicated in Fig. 5, together with the emissivity of this layer, for two compositions. It can be seen from this diagram that, even using a wavelength (3.1μ) at which the absorption coefficient of ammonium perchlorate is very high, the optical method becomes inaccurate at quite modest pressures. The experimental situation is further aggravated by the increase in gas emission as the pressure rises.

Conclusions

It has not been possible to obtain a reasonably accurate measure of the surface temperature of burning ammonium perchlorate above about 60 psia because, even for the infrared optical method, in which a depth of surface about 2μ thick is "seen", the heated zone within the surface becomes too thin. The value of measurements with thermocouples in fast-burning perchlorate mixtures is even more restricted because of the dimensions of the junction and leads.

Up to 60 psia, the variation of surface temperature with ambient pressure is compatible with the condition of equilibrium dissociation at the surface during combustion. The question of the pressure at which this condition breaks down, thus, remains open.

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COMMENTS

Prof. I. Glassman (Princeton University): There appears to be a difference in the sequence of events of the action of the ammonium perchlorate with the fuel, between this paper and that of Cummings et al. (this Symposium p. 1365). One claims that perchloric acid plays a direct reactive role; the other maintains that the ammonium perchlorate decomposes and then reacts as the over-all effect.

Dr. J. Powling: There is no conflict between the two papers. Our paper is concerned with the nature of the primary dissociation of ammonium perchlorate into gaseous ammonia and perchloric acid, while Cummings deals with the flame reactions which would subsequently occur in the products of dissociation, methane substituting for ammonia, to facilitate practical study.

Dr. B. Rabinovitch (United Technology Center): Would the authors comment on the possibility that, in considering the burning of composite fuels, we are dealing with two temperatures of significance, namely, the temperature of the regressing surface and the temperature of the interface between the solid oxidant (ammonium perchlorate) and the polymer fuel?

Dr. J. Powling: In the present studies we have been careful to avoid using a fuel which, by virtue of its high concentration or involatility, would contribute to the infrared emission from the burning surface. In practical composite propellants, however, "the temperature of the regressing surface" might be considered to be an average of the oxidizer and fuel-surface temperatures. I would maintain that the ammonium perchlorate surface temperature remains constant, irrespective of the immediate surroundings; but, at a reacting interface, with a diffusion flame at stoichiometric temperature in between, the binder surface temperature could be higher than average.

Dr. M. Stammer (Aerojet General Corporation): Many combustion catalysts affect the induction time of ammonium perchlorate. For example, the induction time of Cu₂O-containing ammonium perchlorate is—at approximately 260°C—one-third longer than ammonium perchlorate containing ZnO. Therefore, it is possible that the surface temperature is changed, since both additives cause different burning rates in propellants. Another possibility is simply a change in the reaction rates for the reactions occurring during the induction period.

Dr. J. Powling: Apparently "low" surface temperatures are measured by the radiation method, when the ammonium perchlorate contains burning-rate catalysts. However, measurements are complicated by the presence of reaction waves moving across the burning surface. These reaction waves have the appearance of thin zones of enhanced reactivity, moving across the surface and leaving behind areas of quiescent substrate. Temperature traces record the passage of these waves as sharp spikes, but the average temperature of the whole burning surface is lower than that recorded for uncatalyzed ammonium perchlorate.

The degradation mechanism of ammonium perchlorate may well be quite different under the influence of catalysts. For example, we have evidence that rate modifiers, such as copper chromate and calcium carbonate, can significantly alter the products of combustion and the surface temperature to pressure relationship of ammonium perchlorate. These are matters of current study at E.R.D.E., but it is too early for any positive conclusions.

Dr. Marjorie W. Evans (Stanford Research Institute): Could the authors elaborate on the dimensions and velocities of the "surface waves," which were observed on burning ammonium perchlorate, as well as the conditions under which they occur?

Dr. J. Powling: Surface reaction waves are readily observed in ammonium perchlorate compositions containing burning-rate catalysts or relatively involatile fuels. They are prominent at low pressures and burning rates (e.g., at atmospheric pressure) and become more numerous and more rapidly moving as the pressure increases, until they become indistinguishable from "normal" combustion. Their dimensions and velocities have not been measured (although it should be quite easy to do so), but they are seen as thin luminous zones, say about 1 mm wide, expanding over the surface at many times the over-all burning rate. Reference to this mode of reaction was made in a previous publication [ARDEN, E. A., POWLING, J., AND SMITH, W. A. W.: Combust. Flame 6, 21 (1962)].

Dr. J. Wenograd (Princeton University): The role of exothermic reactions, occurring at or slightly below the surface of burning composite propellants, has been considered by a number of investigators. However, the influence of such reactions on the burning mechanism has not been assessed, nor has

their existence been conclusively demonstrated. We have recently observed an interesting combustion phenomenon involving a particular type of composite propellant, which proves the existence of exothermic reactions other than those in the gas-phase flame.

As part of a study of composite propellant burning at subatmospheric pressures, we have found that polysulfide-ammonium perchlorate propellants with fine oxidizer particles are capable of sustaining a combustion wave without the presence of a gas-phase flame. This "flameless combustion" is observed when suitable propellants are burned while the ambient environment is being evacuated. As in the case of other composite propellants, a vacuum is reached where the gas-phase flame is extinguished. However, in the polysulfide propellants, with an oxidizer particle size less than 45μ , a "flameless-combustion" wave continues to propagate. This phenomenon occurs at pressures below about 0.05 atm.

In the "flameless-combustion" regime, the propellant produces quantities of white smoke, and an ash which arises from the surface. Chemical analysis of the products, while incomplete at present, shows that the ash has less carbon and hydrogen

than the original propellant, and considerable ammonium perchlorate, and that the smoke is largely ammonium chloride. Preliminary "flameless-combustion" propagation rates show that the process is quite slow, in the range 0.007 in./sec, and that the rate is inversely related to the oxidizer-particle size. Temperature profiles of "flameless-combustion" waves have been obtained by the use of fine embedded thermocouples, and they indicate that the maximum temperature reached in the wave is less than 300°C at the propellant-ash interface.

Studies of the composite solid-propellant combustion mechanism have been concerned with explaining the acceleration of burning rate by increasing ambient pressure and decreasing oxidizer-particle size. These effects have been presumed to arise through changes in the characteristics of the gas-phase flame. The exothermic surface or condensed-phase reactions, which sustain the "flameless-combustion" waves, should also be evaluated as possible contributors to the over-all combustion mechanism, since they could also be accelerated by increasing pressure and decreasing particle size. Efforts to evaluate the magnitude of such effects in "flameless" and normal combustion are being continued.